THE SYNTHESIS OF 1, 2-DIAROYLBENZENES FROM ACID CHLORIDES AND POLYALKYLBENZENES

BY

WILLIAM REGINALD HATCHARD

B. S., University of Portland, 1941

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FOR THE DEGREE OF DOCTOR OF PHILOSOPHY
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Introduction

It is well known that neither phthalyl chlorides nor o-aroylbenzoyl chlorides can be used in the Friedel-Crafts synthesis to produce o-diaroylbenzenes.[1,2] These compounds yield diarylphthalides. Since phthalide formation, at least with o-aroylbenzoyl chlorides would appear to require cyclization involving an additive reaction of a keto group, it appeared that this type of reaction could be prevented by the introduction of a mesitoyl group. For example, o-mesitoylbenzoyl chloride would hardly be expected to undergo such a ring closure. To test this idea, a study has been made of the condensation of phthalyl chloride with mesitylene, isodurene, durene, *sym*-triethylbenzene and *sym*-triisopropylbenzene.

Discussion and Results

Phthalyl chloride has been found to condense with mesitylene in the presence of aluminum chloride to give a good yield of o-dimesitoylbenzene, m.p. 236°. Moreover, the same compound was obtained from o-mesitoylbenzoyl chloride. The identity of the new diketone was confirmed by the discovery that it could be made also by the condensation of mesitylmagnesium bromide with phthalyl chloride and with o-mesitoylbenzoyl chloride. These observations definitely exclude the phthalide structure.

o-Dimesitoylbenzene was unaffected by treatment with strong alkali and failed to undergo cleavage when heated with syrupy phosphoric acid.[3] It could be recovered after treatment with phenylmagnesium bromide. Treatment of the diketone with metallic sodium in hot amyl alcohol gave a mixture of reduction products from which no pure compound could be isolated. When a mixture of the diketone and alcoholic potassium hydroxide was boiled for twenty hours in the presence of zinc dust, the diketone was converted to 1,3-dimesityl-1,3-dihydroisobenzofuran, m.p. 205°. Treatment of the diketone with zinc and alcoholic potassium hydroxide for only a short time[4] or with zinc in glacial acetic acid[5] gave mixtures of the starting material, the dihydroisobenzofuran, and a more soluble product. This more soluble product, which was isolated from the mother liquors in

an impure condition, was yellow and exhibited a blue fluorescence, indicating that it was probably 1,3-dimesitylisobenzofuran. When *o*-dimesitoylbenzene was hydrogenated at 175° under 2000 pounds pressure in the presence of Raney nickel catalyst, it was converted to α,α-dimesityl-*o*-xylene, m.p. 208°. The structure of this new hydrocarbon was established by an independent synthesis. It was produced by the condensation of α^2-chloroisodurene with the Grignard reagent prepared from α-mesityl-*o*-bromotoluene. The mesityl bromotoluene which melted at 69.5-70° was prepared by condensing *o*-bromobenzyl bromide with mesitylene in the presence of aluminum chloride.

Phthalyl chloride has been condensed with other polyalkylbenzenes to produce the following diketones: *o*-diduroylbenzene, m.p. 268-270°; *o*-diisoduroylbenzene, m.p. 260-261°; *o-bis*-(2,4,6-triethylbenzoyl)-benzene, m.p. 77-78°. A similar condensation with 1,3,5-triisopropylbenzene gave only an intractable oil. Considerable quantities of heavy, viscous oils were obtained also in the condensations.

It was found that the synthesis could be extended to hexahydrophthalyl chloride. It was prepared from *trans*-hexahydrophthalic acid[6] and, accordingly, was assigned the *trans* configuration. The acid chloride was condensed with benzene, mesitylene, durene and isodurene to yield the corresponding *trans*-1,2-diarylcyclohexanes: dibenzoyl-, m.p. 113-113.5°;dimesitoyl-, m.p. 234.5-235.5°; diduroyl-, m.p. 149.5°; diisoduroyl- m.p. 189°. That the condensation products were diketones and not phthalides was shown easily by their conversion to 1,3-diaryl-4,5,6,7-tetrahydroisobenzofurans by treatment with a mixture of sulfuric and acetic acids. Although no tetrahydroisobenzofurans have been reported previously, they are formed in the same way as the dihydroisobenzofurans.[4]. The following tetrahydroisobenzofurans were prepared: diphenyl-, m.p. 97.5°; dimesityl-, m.p. 135-136°; diduryl-, m.p. 139.5-140°; diisoduryl-, m.p. 194-195°.

trans-1,3-Dimesitoylcyclohexane was found to react with the Grignard reagent in an anomalous manner. When the diketone was treated with ethylmagnesium bromide, no gas was evolved and a new compound was obtained by hydrolysis of the reaction

mixture. The new compound melted at 135.5-136° and had the composition of $C_{28}H_{34}O_3$. The same compound was produced when the diketone was caused to react with methylmagnesium iodide. No plausible structure of this compound has been formulated.

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Vita

The author was born in Sheerness, England, on October 20, 1919, and came to the United States in 1922. He became a citizen of this country in 1939. He attended the public schools of Portland, Oregon, graduating from Washington High School in June, 1937. His undergraduate training was obtained at the University of Portland where he was granted the Bachelor of Science degree in June, 1941. In the Fall of that year he entered the graduate school of the University of Illinois where he held a teaching assistantship from September, 1941 to July, 1943. He has been employed by that institution as a special research assistant since July, 1943.

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